AND LUBRICANT INTERFERANT
SUBSTANCES

AFLRL REPORT NO. 79

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|            | ingric buritants  |  |
| 7          | A variety of chemicals were evaluated as poten and/or lubricant degradants in spark and compr Several materials showed good to excellent pot ignition interference. None of the materials | ession ignition engines.                                       |
|            | short-term lubricant interference. High expan foam was investigated as a medium for dispensicals. Propane was found to be compatible with   | sion ratio water based   |
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#### DEVELOPMENT OF ENGINE AND LUBRICANT INTERFERANT SUBSTANCES

#### INTRODUCTION

The U.S. Army Fuels and Lubricants Research Laboratory (AFLRL), a government-owned contractor operated facility located at Southwest Research Institute (SwRI) in San Antonio, Texas, has conducted an exploratory study to determine chemicals which act as engine/lubricant interferant substances. The basic objective was to define or develop a chemical agent which when introduced in the air in low concentrations will pass through an engine's air filter and cause extreme power loss or failure to reciprocating piston internal combustion engines in a reasonably short period of time. The program was divided into the following three work packages:

- 1. Interference in engine operation by modification of fuel ignition and/or combustion characteristics to degrade engine power output.
- 2. Interference in engine operation by causing significant lubricant degradation resulting in loss of engine power.
- 3. A feasibility demonstration based on the development of a high expansion ratio water based foam as a method of carrying and dispensing an interferant substance.

#### SUMMARY

Over fifty chemicals were evaluated as potential combustion modifiers and/or lubricant degradants in both spark ignition (SI) and compression ignition (CI) single-cylinder engines. Both gaseous and liquid agents at ambient conditions were investigated. Several of the materials evaluated showed good to excellent potential for combustion and/or

ignition interference. None of the chemicals investigated showed dramatic short-term lubricant interference. Finally a feasibility demonstration was conducted for a MERADCOM representative using propane  $(C_3H_8)$  as the interferant substance in a high expansion ratio water based foam. Propane was chosen as the interferant substance because of its excellent engine interference at low concentrations, excellent compatibility with high expansion ratio water based foam and because it is relatively inexpensive and readily available. A one-half ton pickup truck powered by an SI engine was unable to pass through a berrier of propane containing foam.

#### DISCUSSION

# A. Combustion/Ignition Interferant Agent Screening

The ability of candidate chemical agents to function as combustion/ignition interferant agents was determined using single-cylinder spark ignition (SI) and compression ignition (CI) engines. The agent was mixed with intake air in a special mixing can, and then the mixture passed through a standard automotive pleated paper air filter.

#### Equipment and Materials

The test engines were a single-cylinder air cooled spark ignition Briggs and Stratton of 0.38 1 (22.9 in.<sup>3</sup>) displacement and a single-cylinder water cooled compression ignition Petter of 0.66 1 (40.2 in.<sup>3</sup>) displacement. The SI engine had a compression ratio (CR) of 5.4:1 while the CI engine had a CR of 16:1. Complete details of the two test engines are shown in Table 1. The engines were mounted on stands in a test cell and instrumented to determine the following:

Engine speed (RPM)
Engine load

TABLE-1
Test Engines

|                      | Petter      | Briggs-Stratton |  |
|----------------------|-------------|-----------------|--|
| Type Ignition        | Compression | Spark           |  |
| Cylinder No.         | 1           | 1               |  |
| Cooling              | Water       | Air             |  |
| Displacement, liters | 0.66        | 0.38            |  |
| Bore, cm             | 8.73        | 7.62            |  |
| Stroke, cm           | 11.00       | 8.26            |  |
| Compression Ratio    | 16:1        | 5.4:1           |  |
| Rated Power          | 5.6 kW      | 6.0 kW          |  |

TABLE-2
Test Lubricant (REO 204, 30 Grace)

|                     | ASTM Method | Properties  |
|---------------------|-------------|-------------|
| Description         |             | MIL-L-2104C |
| API Gravity         | D287        | 27.4        |
| Viscosity, cS @ 38c | D445        | 12.24       |
| Viscosity, cS @ 99c | D445        | 119.4       |
| Sulfated Ash, %w    | D874        | 0.85        |
| Total Acid No.      | D664        | 1.53        |
| Total Base No.      | D2896       | 5.36        |

Intake vacuum
Exhaust temperature
Ambient temperature
Intake charge temperature
Intake air flow - Rotometer
Agent flow - Rotometer
Oxygen content of exhaust

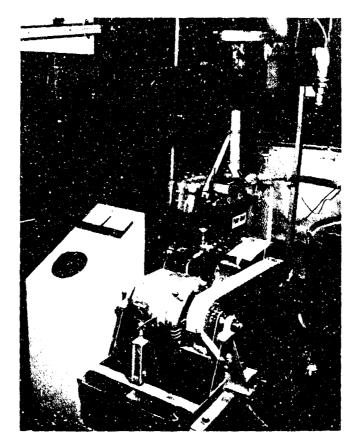
The engine installations are shown in Figure-1.

The engine lubricant used in both engines was a MIL-L-2104C, 30 grade reference oil typical of motor oils found in service. Properties of the test lubricant are shown in Table - 2. The fuels used were unleaded gasoline (VV-G-001690A) in the SI engine and a reference No. 2 diesel oil in the CI engine. The test fuel properties are shown in Table 3.

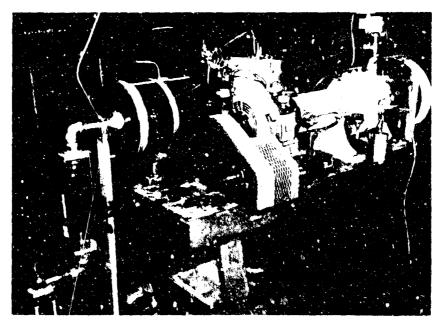
#### **PROCEDURE**

Engine runs were made to develop suitable operating conditions and to develop an evaluation procedure. The operating conditions for evaluating engine interferants are shown in Table 4. The technique employed to evaluate engine interferants consisted of operating the engines at stabilized, loaded conditions (2000 RPM for SI and 1800 RPM for CI) and then introducing measured amounts of interferant which was mixed with the intake air charge in a special mixing can. The mixture then passed through a standard automotive pleated paper type air filter and into the engine's intake system for delivery to the cylinder. The amount of interferant being introduced was increased until present in sufficient quantity to interfere with the combustion process as evidenced by loss of engine speed, reduced load, and eventual engine stoppage. Gaseous agents were metered directly into the mixing can, while liquid interferants were atomized to a very fine mixt by compressed air and sprayed into the can for mixing with the intake air charge. The amount of

FIGURE-1
Engines Mounted on Test Stands



Petter (CI)



Briggs Stratten (SD)

TABLE-3
Test Fuel Properties

|                                 | ASTM Method   | C.I.              | <u>S.I.</u>                       |
|---------------------------------|---------------|-------------------|-----------------------------------|
| Туре                            |               | DF-2<br>Reference | Unleaded Gasoline<br>VV-G-001690A |
| API Gravity                     | D287<br>D1266 | 33.3°<br>0.44     | 57.5°<br>0.004                    |
| Sulfur, %wt<br>Distillation, °C | D86           | 0.44              | <b>V</b> •001                     |
| IBP                             |               | 210               | 31                                |
| 50%                             |               | 268               | 106<br>162                        |
| 90%<br>EP                       |               | 315<br>362        | 182                               |
| Lead, g/l (g/gal)               |               |                   | 0.002 (0.008)                     |
| Research Octane No.             | D2699         |                   | 93.2                              |

TABLE-4
Operating Conditions for Interferant Evaluation

|  | <u>C.I.</u>          | <u>S.I.</u>     |
|--|----------------------|-----------------|
| Engine Speed, RPM  | 1 <b>8</b> 00<br>5.9 | 2000<br>6.4     |
| Load, kg Air Intake, m <sup>3</sup> /min Exhaust Temperature, °C | 0.59<br>290-340      | 0.18<br>525-540 |

gaseous interferant which caused combustion and/or ignition interference is reported as percent volume interferant, and percent weight interferant. These percentages are calculated as follows:

Liquid interferant agents are reported as weight percent interferant as shown above, and as cc interferant/m<sup>3</sup> intake air.

#### **RESULTS**

The results are presented in two main groups: (1) gaseous interferants and (2) liquid interferants, with several classes of each group represented. The effects of materials in each group on SI and CI engine operations are examined.

## Gaseous Interferants

The gaseous interferants selected for evaluation were for the most part heavier than air so that when dispensed would lay near the ground. Gaseous interferants were divided into the following general classes:

- Inerts
- Halons
- Fuels
- Others

The results of all gaseous interferant evaluations are shown in Table 5.

The inert gases evaluated included argon, carbon dioxide and sulfur hexafluoride. Copious amounts of argon and carbon dioxide were needed

TABLE-5 Gaseous Engine Interferants

| Interferant  | Formula  | Interfera<br>Compression<br>% Vol.           | nt Needed<br>Ignition<br>% wt.                           | Spark I % Vol.                              | Engine<br>gnition<br>% wt.                   |
|--|--|--|--|---|--|
| Inerts Argon Carbon Dioxide Sulfur Hexafluoride Halons   | Ar<br>CO <sub>2</sub><br>SF <sub>6</sub>   | 44<br>24<br>6                                | 49<br>32<br>24   | 20<br>13<br>8                               | 23<br>23<br>33                               |
| Halon 14 Halon 26 Halon 38 Halon 13 Halon 121 Halon 131 Halon 122 Halon 251 Halon 242 Halon 1301 | CF4<br>C <sub>2</sub> F6<br>C <sub>3</sub> F6<br>CHF3<br>CHC1F <sub>2</sub><br>C C1 F <sub>2</sub><br>C C1 <sub>2</sub> F <sub>2</sub><br>C <sub>2</sub> C1 F <sub>5</sub><br>C <sub>2</sub> C1 <sub>2</sub> F <sub>4</sub><br>C Br F <sub>3</sub> | 9<br>5<br>4<br>14<br>15<br>10<br>9<br>6<br>5 | 23<br>19<br>22<br>27<br>36<br>29<br>31<br>25<br>24<br>36 | 11<br>4<br>11<br>4<br>7<br>3<br>6<br>2<br>2 | 18<br>23<br>24<br>11<br>22<br>12<br>24<br>11 |
| Fuels Acetylene Butane   | $C_2H_2$ $C_4H_{1.0}$  | 3 a<br>3 b                                   | 3 <sup>8</sup><br>9                                      | 16<br>4                                     | 14<br>8                                      |
| Others Oxygen Nitrous Oxide Sulfuryl Fluoride Hydrogen Bromide Boron Trifluoride                 | O <sub>2</sub><br>N <sub>2</sub> O<br>SO <sub>2</sub> F <sub>2</sub><br>HBr<br>BF <sub>3</sub>   | >21<br>30<br>9<br>>15                        | >23<br>40<br>26<br>                                      | 12 <sup>a</sup><br>45<br>10<br><br>12       | 14 <sup>a</sup><br>55<br>30<br><br>24        |

a = Severe preignition, stopped test to prevent engine damage.
 b = Engine quit, some preignition observed.

TABLE-6

# CFR Single Cylinder Engine

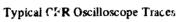
| a                 | 7 to 28           |
|-------------------|-------------------|
| Compression Ratio | 8.26              |
| Bore, cm          | 11.43             |
| Stroke, cm        | 612               |
| Displacement, cc  | 900 RPM           |
| Engine Speed      | Besch imjection   |
| Fuel Delivery     | pump and injector |

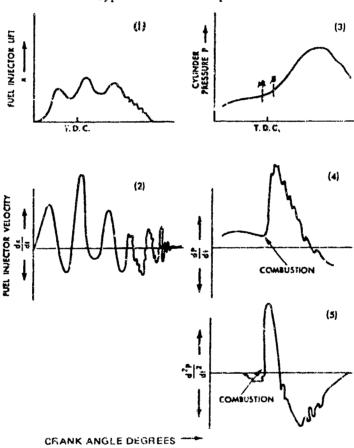
to stop either the SI or CI engine. Sulfur hexafluoride was much more effective on a volume basis in both engines. The inert gases appeared to function primarily by suffocation (oxygen displacement) with some heat sink effects evident in the CI engine. Using argon, it was found that to stop the engine, the oxygen content of the intake air had to be lowered to approximately 17% vol in the SI engine and 12% vol in the CI engine.

The Halons (halogenated carbon compounds) were evaluated because they were heavier than air, nontoxic and most had fairly good availability. Halon 1301 (CBrF<sub>3</sub>) is currently being used as the active ingredient in a commercial fire extinguishing system. Halon 242  $(C_2C1_2F_4)$  was the most overall effective gaseous Halon engine interferant stopping the SI engine with 2% vol (11% wt) and the CI engine with 5% vol (24% wt). Halon 26  $(C_2F_6)$  and Halon 38  $(C_3F_8)$  were also very effective. Halon 1301 (CBrF $_q$ ) was effective in the SI engine, but not as good in the CI engine. In the CI engine, all fully halogenated Halons (no hydrogen present) were effective in stopping the combustion process. Most Halons stopped the CI engine between 5-10% vol (20-30% wt) which indicated a mechanism other than oxygen suffocation was involved because the intake air charge still contained sufficient oxygen for combustion. Approximately 18 to 19% vol oxygen was available which far exceeded the level of 12% vol oxygen which was required to stop the engine when argon was the interferant.

A brief investigation of the mechanism of Halon engine interference was conducted, as an aid to selecting other interferants and to help in choosing an optimum Halon. This was achieved by determining the effect of compression ratio (CR) on the amount of interferant needed. A single-cylinder CFR compression ignition engine which has a variable CR was used. Table 6 gives the details of this engine. The engine was instrumented with an oscilloscope to monitor fuel injection, cylinder compression ignition delay and peak pressure rise. Figure 2 shows plots of typical diesel combustion oscilloscope traces for detection of injection and combustion. Four gaseous Halon materials were tested at various

FIGURE-2





Detection of Injection and Combustion.

CR's, and as illustrated in Figure 3, as the CR increased the amount of Halon required to stop the engine increased. As the amount of gaseous Halon introduced was increased, the following observations were noted:

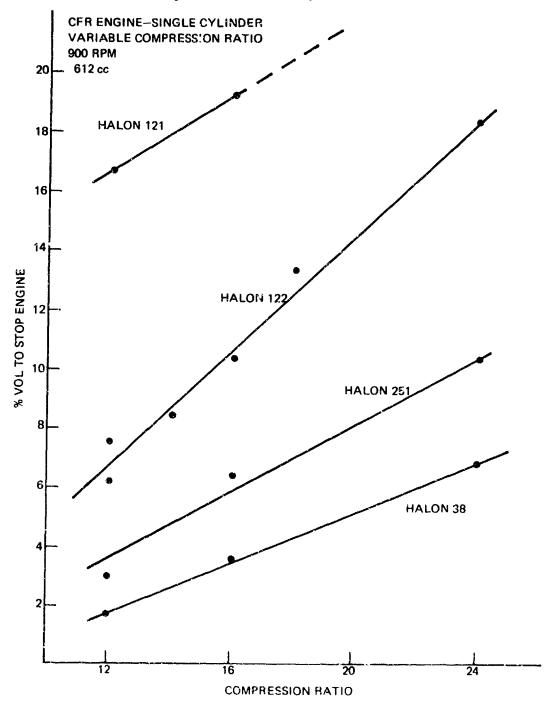
- compression pressure slightly decreased
- significant ignition delay occurred
- peak pressure increased

These phenomena were further investigated by instrumenting the CFR diesel with equipment capable of recording combustion heat release data. Selected gaseous Halons were mixed with the intake air and the combustion event was monitored in an attempt to understand why the interferants were halting combustion. The results indicate that the Halon interferants were acting as "heat sinks" during the compression stroke (noted by the decreasing compression pressures in this engine from 2928 to 2480 kN/m² absolute), thus causing significant ignition delay. As the volume of interferant was raised to the engine fail point, ignition delay was extended 10-15 crank angle degrees; therefore, the piston had started down in the power stroke, cooling was taking place and thus the fuel/air-interferant charge could not ignite. No evidence to indicate any chemical inhibition of the combustion event was observed. Were the engine stopping without significant ignition delay, chemical inhibition would be suspect.

The next subgroup of gaseous interferants evaluated were fuels. Acetylene ( $C_2H_2$ ) was very effective in causing the engine interference, but only moderately effective in the SI engine. In the CI engine, acetylene caused the engine to run erratic with severe prelignition, and the test was terminated at 3% vol acetylene to prevent permanent engine damage. This is believed to be directly related to the autoignition temperature of acetylene (335°C). Also of significance, the engine operator noted that restart of the engine was extremely difficult. Butane ( $C_4H_{10}$ ) was also very effective in stopping both the CI and SI engines at low concentrations. In fact, based on the excellent interference caused by butane, propane ( $C_3H_8$ ) a close relative of butane, was selected as the interferant for use in the foam demonstration.

FIGURE-3

Compression Ratio Versus Required Halon Interferant



The subgroup "other" gaseous interferants contained a wide range of materials from oxygen to corrosive agents such as hydrogen bromide (HBr) and boron trifluoride (BF<sub>3</sub>). Only sulfuryl fluoride (SO<sub>2</sub>F<sub>2</sub>) showed significant engine interference, and it is considered somewhat toxic despite being colorless, odorless and non-corrosive.

Considering all the gaseous interferants, in both CI and SI engines, the "fuels type" such as butane and acetylene were very effective at low volume and weight percentages. Selected Halons such as Halon 38 and Halon 26 were very effective in both engine configurations at rather low volume percentages, but suffered a penalty on the weight basis because of their high density.

## Liquid Interferants

A wide variety of liquid interferants of several different chemical classes were evaluated. The procedure involved atomizing the liquid with compressed air and spraying this mixture into the intake air stream. We were looking for materials which were very effective at low concentrations; that is materials which were more effective at causing engine interference than the "fuels type" gases or the gaseous Halons. In some cases, at very high liquid flow rates some liquid was found in the mixing can after the test. This meant that not all the indicated liquid flow was ingested by the engine. This is not considered significant to the project objectives because it occurred only at very high liquid flow rates, and these agents were relatively ineffective at causing engine interference. Liquid interferants were divided into the following general classes:

- Halons
- Perfluoro compounds
- Amines
- Phosphorus compounds
- Sulfur compounds
- Others

The results of all liquid interferant evaluations are shown in Table 7.

Fourteen liquid Halon compounds including three iodine containing materials were evaluated for engine interference. On a weight basis, only Halon  $233\ (C_2Cl_3F_3)$  was as effective as the better gaseous Halons in both the CI and SI engines. Several of the liquid Halons gave good SI engine interference at weight percentages equivalent to the better gaseous Halons, but did not show exceptional CI engine interference. Halon  $10001\ (CH_3I)$  was significant because it was the only Halon which caused CI engine preignition (at 20% wt). Additionally, it stopped the SI engine at 11% wt. However, a noxious purple gas was formed during combustion.

Because the Halons which contained mostly or entirely all fluorine atoms as the halogen entity seemed to be the most effective in promoting engine interference, several perfluoro compounds (totally fluorinated) were evaluated. Only trifluoroacetic acid (CF<sub>3</sub>COOH) at 13% wt in the CI engine showed any significant engine interference at a reasonable weight percentage. This investigation illustrated that molecules with a large number of fluorine atoms present are not necessarily effective engine interferants.

Amine compounds were evaluated as engine interferants because it was reported in the literature that certain aliphatic amines function as gas phase oxidation inhibitors. The lower molecular weight amines up through n-butylamine ( $C_4H_9NH_2$ ) were very effective in stopping the SI engine and caused very severe preignition in the CI engine at low concentrations - typically at 2 to 5% wt. The expected combustion interference from oxidation inhibition was not observed, but the severe preignition in the CI engine at low concentration, plus the stoppage of the SI engine at low concentration make the low molecular weight amines very desirable as engine interferants. Higher molecular weight amines were investigated, but caused no CI engine preignition and were not significantly effective in the SI engine.

Phosphorus containing materials were investigated as engine interferants because of their use in fire resistant materials. None of the three

TABLE-7
Liquid Engine Interferants

|                       |   | Interferant Needed to Stop Engine |            |          |                            |
|-----------------------|---|-----------------------------------|------------|----------|----------------------------|
|                       |   |                                   | <u>.I.</u> | % wt.    | S.I. cc/m <sup>3</sup> Air |
| Interferant           | Formula   | % wt.                             | cc/m Air   | e wt.    | 00/11/                     |
|                       |   |                                   |            |          |                            |
| Halons                | CClu  | 28                                | 286        | 14       | 113                        |
| Halon 104             | C <sub>2</sub> C <sub>1</sub> <sub>3</sub> F <sub>3</sub>     | 21                                | 194        | 20       | 184                        |
| Halon 233             | CH <sub>2</sub> BrCl  | 38                                | 357        | 8        | 49                         |
| Halon 1011            | CH <sub>2</sub> Br <sub>2</sub>                               | >22                               | >127       | 19       | 106                        |
| Halon 1002            | _   | >32                               | >191       | Spec and |                            |
| Halon 1003            | CHBr <sub>3</sub>   | >29                               | >200       | 21       | 134                        |
| Halon 1202            | CBr <sub>2</sub> F <sub>2</sub>                               | >30                               | >220       |          |                            |
| Halon 1103            | CBr <sub>3</sub> F  | >32                               | >180       |          |                            |
| Halon 2004            | C <sub>2</sub> H <sub>2</sub> Br <sub>4</sub>                 | >28                               | >210       | 9        | 53                         |
| Halon 2402            | C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>                 | >22                               | >138       | 16       | 92                         |
| Halon 3602            | C <sub>3</sub> Br <sub>2</sub> F <sub>6</sub>                 |                                   | - 100      | 17       | 145                        |
| Halon 362             | C3Cl2F6   | 20 <sup>a</sup>                   | 127        | 11       | 64                         |
| Halon 10001           | CH₃ I   | 20                                | >170       | >33      | >600                       |
| Halon 10002           | CH <sub>2</sub> I <sub>2</sub>                                | >33                               | >160       |          |                            |
| Halon 37001           | C <sub>3</sub> F <sub>7</sub> I                               | >24                               | >100       |          |                            |
| Perfluoro Compounds   |   |                                   |            |          |                            |
| Perfluoro-n-butyl-    | CF = CF - CF = C  |                                   |            | 25       | 380                        |
| perfluorofuran        | 1-0-1   | ~-                                |            | >25      | >200                       |
| Perfluorotributyl-    | (C4F9)3N  | >29                               | >251       | 723      | 200                        |
| amine                 |   | > 20                              | >258       |          | count made which           |
| Perfluorokerosene     |   | >29                               | 113        | >29      | >300                       |
| Trifluoroacetic acid  | CF3COOH   | 13                                | >185       | >40      | >525                       |
| Heptafluorobutyric    | $CF_3(CF_2)_2COOH$  | >21                               | /103       |          |                            |
| acid                  |   |                                   |            |          |                            |
| Amines                |   |                                   | 250        | >40      | >1000                      |
| n-hexylamine          | C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>                | 14 a                              | 250        | 8        | 138                        |
| di-n-propylamine      | $(C_3H_7)_2NH$  | 1,5 <sup>a</sup>                  | 25         | 9        | 159                        |
| triethylamine         | $(C_2H_5)_3N$   | 3                                 | 53         | 30       | 600                        |
| triallylamine         | $(CH_2 = CHCH_2)_3N$  | 4 4                               | 56         |          | 131                        |
| n-propylamine         | C3H7NH2   | 3<br>4<br>4<br>5<br>4<br>4        | 81         | 8        | 152                        |
| n-butylamine          | C4H9NH2   | 4 <sup>a</sup>                    | 64         | 9        | >750                       |
| N, N-dimethyldodecyl- | CH2 (CH2) 13N(CH3) 2  | 16                                | 275        | >30      | > / 30                     |
| amine                 | 0113 (2112) 11  |                                   |            |          | 424                        |
| N, N-dimethylcyclo-   | CH <sub>2</sub> (CH <sub>2</sub> ) 4CHN (CH <sub>3</sub> )    | 2 24                              | 438        | 24       | 424                        |
| N, N-dimetry teyers   |   | -                                 |            |          |                            |
| hexylamine            |   |                                   |            |          | S F 0 0                    |
| Phosphorus Compounds  | (C4H9) 3PO4   | >24                               | >375       | >30      | >500                       |
| Tributylphosphate     | (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PO <sub>4</sub> | 12                                | 170        | >30      | >600                       |
| Triethylphosphate     | $(C_2H_5)_3PO_3$  | >16                               | >270       | 19       | 300                        |
| Triethylphosphite     | (4.2312)31.43   | <del>-</del>                      |            |          |                            |
| Sulfur Compounds      | (CH <sub>3</sub> ) <sub>2</sub> S0                            |                                   |            | >28      | >400                       |
| Dimethylsulfoxide     | [(CH3) 250<br>[(CH3) 250                                      | $\overline{11}^{a}$               | 155        | >30      | >700                       |
| t-hutyldissulfide     | [(CH <sub>3</sub> ) <sub>3</sub> CS-] <sub>2</sub>            | >24                               | >220       | 13       | 106                        |
| Thionylchloride       | SOC12   | - 4- T                            |            |          |                            |

a = Severe preignition, stopped test.

TABLE-7 (Cont.) Liquid Engine Interferants

|  |   | Inte                          | erferant Needed               | to Sto | p Engine                                |
|--|---|-------------------------------|-------------------------------|--------|---|
| Interferant                                | Formula   | % wt.                         | C.I.<br>cc/m <sup>3</sup> Air | % wt.  | $\frac{\text{S.I.}}{\text{cc/m}^3}$ Air |
| Others                                     |   |                               |                               |        |   |
| Bromobenzene                               | C <sub>6</sub> H <sub>5</sub> Br                                    | 19                            | 177                           | >40    | >590                                    |
| Propylacetate                              | CH <sub>3</sub> COOC <sub>3</sub> H <sub>7</sub>                    | 13 <sup>a</sup>               | 198                           | 32     | >600                                    |
| t-butylacetate                             | CH <sub>2</sub> COOC (CH <sub>3</sub> ) <sub>3</sub>                | 11 <sup>a</sup>               | 162                           | 10     | 148                                     |
| Acetone                                    | (CH <sub>3</sub> ) <sub>2</sub> CO                                  | 10 <sup>a</sup>               | 159                           | 4      | 67                                      |
| Methanol                                   | CH <sub>3</sub> OH  | 11                            | 187                           | >27    | >500                                    |
| Ethanol                                    | C <sub>2</sub> H <sub>5</sub> OH                                    | 10                            | 155                           | >24    | >450                                    |
| Isopropanol                                | (CH <sub>5</sub> ) <sub>2</sub> CHOH                                | 16<br>4a                      | 286                           | 29     | >600                                    |
| n-heptane                                  | C 7H14  |                               | 60                            | 9      | 166                                     |
| Isooctane                                  | (CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>4</sub> C | H <sub>3</sub> 4 <sup>a</sup> | 74                            | 8      | 138                                     |
| Water                                      | H <sub>2</sub> O  | >23                           | 340                           | >30    | >600                                    |
| 30%v Hydrogen Peroxide                     | H <sub>2</sub> O <sub>2</sub> in H <sub>2</sub> O                   | >23                           | >340                          |        |   |
| Ethyl Motor Mix No. 1 (61% tetraethyllead) |   | 2                             |                               |        |   |
| Tetrahydrofuran                            | $C_4H_4O$   | 5 a.                          | 74                            | 9      | 131                                     |
| Pyridine                                   | C <sub>5</sub> H <sub>5</sub> N                                     | 14 <sup>a</sup>               | 184                           | 27     | >430                                    |
| Piperidine                                 | C <sub>5</sub> H <sub>11</sub> N                                    | $\frac{1}{6}$ a               | 88                            |        |   |
| Pyrrolidine                                | C4H9N   | 5 <sup>a</sup>                | 67                            |        |   |
| Germanium tetrachloride                    | GeCl4   | >29                           | >254                          |        |   |

a = Severe preignition, stopped test.b = Erratic combustion.

phosphorus containing materials were effective in both the CI and SI engines at reasonable concentrations. Triethylphosphate did stop the CI engine at 12% wt, but was not effective in the SI engine.

Three sulfur containing compounds were evaluated. None caused engine interference in both CI and SI engines at low concentrations. In the CI engine t-butyldisulfide  $[(CH_3)_3CSSC(CH_3)_3]$  did cause preignition, but this occurred at 11% wt which was higher than most preignition agents.

The group "others" included a wide variety of liquids ranging in composition from water to alcohols to hydrocarbons to nitrogen containing heterocycles and even tetraethyllead. Because of the vast nature of this group, only materials which were very effective in both the CI and SI engines or very exceptional in one of the engines will be discussed. Acetone  $[(CH_3)_2CO]$  was reasonably effective in the CI engine causing preignition at 10% wt and also stopped the SI engine at 4% wt. Normal heptane  $(C_7H_{14})$  and isooctane  $[(CH_3)_2CH(CH_2)_4CH_3]$ , both caused severe CI engine preignition at 4% wt and stopped the SI engine at 9 and 8% wt respectively. Chemically, these are both close relatives of n-butable but of greater molecular weight.

Tetrahydrofuran  $C_4H_4O$  caused severe CI preignition at 5% wt and stopped the SI engine at 9% wt. Piperidine  $(C_5H_{11}N)$  and pyrrolidine  $(C_4H_9N)$ , two nitrogen heterocyles caused severe CI preignition at 6 and 5% wt respectively, but were not evaluated in the SI engine. An Ethyl Motor Mix No. 1 (61% tetraethyllead) antiknock additive package was evaluated in the CI engine. At 21% wt, this material caused very erratic combustion and engine restart was difficult.

Considering all the liquids evaluated, the most promising overall engine interferants for both CI and SI engines were the low molecular weight amine compounds, acetone, tetrahydrofuran, n-heptane and isooctane. Severe preiginition was the most common mechanism for CI engine interference by liquid agents at relatively low weight percentages.

## B. Lubricanc Interferant Agents

The test lubricant used for all screening tests was a MIL-L-2104C, 30 grade, reference oil whose properties were presented in Table 2. None of the gaseous or liquid agents tested as combustion interferants (Tables 5 and 7) showed any dramatic short-term lubricant interference. Adequate engine lubrication was maintained at all times for both the CI and SI engine. Engine oil was drained at the end of each test day and fresh oil was recharged so that any potential short-term lubricant interference could be detected immediately.

Because acidic combustion products (HC1 and/or HF) were formed with Halons present in the intake air charge, changes in the acidic content and reserve alkalinity of the lubricant were determined. Typical used oil analyses are shown in Table 8.

Table 8 Used Oil Analyses

|       |      |     | ASTM       | New        | 10 mg/m 1400.000.000 pt 1400.000 pt 1400.0 | Used Oil    |             |
|-------|------|-----|------------|------------|--|-------------|-------------|
|       |      |     | Method No. | <u>0i1</u> | <u>C.I1</u>  | <u>C.I2</u> | <u>S.I1</u> |
| Total | Acid | No. | D664       | 1.53       | 2.10   | 6.65        | 2.33        |
| Total | Base | No. | D2896      | 5,36       | 4.82   | 1.84        | 5.36        |

The accumulation of acidic combustion products in the motor oil is evident in both the CI and SI engine. The total base number which is representative of remaining acid neutralizing ability of the oil, is reduced in the CI used oil samples, and both CI and SI used oil samples showed increased acidic content. This condition might lead to long-term lubricant interference, but no short-term interference was observed.

## C. Development of Ingestant Dispensing System

A separate phase of this project involved the development of a dispensing system for the engine ingestants. This phase was conducted

concurrently with the laboratory investigation; therefore, it was unknown whether the most effective engine ingestants would be in the form of a gas, liquid, or solid. It was established that the engine air intake was the only access to the engine that would be allowed. Therefore, the dispensing system had to be capable of making liquid and powder ingestants available to the inlet ports on the military tanks which are approximately 1.2 to 1.5 M above the ground level. In addition, the dispensing system had to be designed to contain gaseous engine ingestants in the proper concentrations so that they would be effective against the tanks. After reviewing the requirements, it was decided that the most feasible method of dispensing ingestants in any of the three forms was in association with an aqueous foam.

Commercially-available aqueous foam generating units are available from a number of different sources. Large single units are capable of generating as much as 2080 cubic meters of foam per minute. The foam that is generated is obtained by introducing low concentrations of surfactants into a stream of water using an aspirator principle. This surfactant is mixed with the water by the turbulent action of the water flow. This mixture is then sprayed on a fine screen wire through which high velocity air is blown, forming the low density aqueous foam. This type of equipment is used by fire departments to fight fuel fires.

#### Surfactant Selection

Personnel at SwRI have had a great deal of experience with aqueous foam systems as a result of work performed on a number of different projects. Many different surfactant systems have been evaluated which are capable of generating high-expansion foam. One project on which a significant amount of investigation of surfactants was conducted involved the development of an aqueous non-conductive foam for the Apollo space capsule. As a result of this extensive background, only a minimum number of surfactants had to be investigated.

Table 9 lists 15 of the surfactants that were examined during the early stages of this program. The investigation involved placing 500

|                | Surfactant                 | Manufacturer         | Type & Class  | Ratio, %<br>Surfactant<br>Water | Approximate<br>Expansion<br>Ratio | Foam<br>Stability* |
|----------------|----------------------------|----------------------|---|---------------------------------|-----------------------------------|--------------------|
| 4              | Ammonium Oleate            | Several              | Anionic - Oleaic Acid and   | 3                               | 25:1                              | Good               |
| ci             | Sodium Oleate              | Several              | Anionic - Oleaic Acid and   | 3                               | 25:1                              | Good               |
| ių,            | Sodium Tallate             | Several              | Anionic - Tall Oil Acid and                                       | 8                               | 25:1                              | Poog               |
| +;             | Ammonium Tallate           | Several              | Anionic - Tall Oil Acid and                                       | 3                               | 25:1                              | Poog               |
| 'n             | Ammonium Casinate          | Several              | Animonium nyaroxide<br>Anionic - Casine and Ammonium<br>Hydroxide | м                               | 25:1                              | Good               |
| 9              | Duponal C                  | DuPont               | Anionic - Sodium Lauryi   | 7                               | 100:1                             | poog               |
| t ··           | Mearl High Expansion       | Mearl Chemical       | Nonionic - Protein Hydroxly-                                      | 82                              | 100:1                             | Good               |
| άci            | Mearl Non-Conducting       | Mearl Chemical       | Nonionic - Alkyl Arylester of                                     | М                               | 100:1                             | Good               |
| 9.             | Duponal EP                 | DuPont               | Folypropieme Oxide<br>Anionic - Fatty Alcohol                     | 2                               | 100:1                             | Fair               |
| 0              |                            |                      | Nonionic - Alkylaryl Polyether                                    | 3                               | 250:1                             | Fair               |
|                | Triton X 100               | Rohm & Hass Co.      | Nonionic - Iso-octyl Phenyl                                       | 8                               | 250:1                             | Fair               |
| C1             | Triton X 151               | йоһт & Hass Co.      | Anionic - Blend of Alkyaryl Polyether Alcohols with               | ю                               | 250:1                             | Fair               |
| 9 <del>7</del> | NCF 865-16J<br>Light Water | Mearl Chemical<br>3M | Nonionic - Unknown<br>Unknown - Flucrocarbon Surfac-              | 1.5                             | 250:1<br>500:1                    | poog<br>200g       |
| 13.            | Hi-Ex                      | Walter Kidde Co.     | Nonionic - Unknown  | 1.5                             | 1000:1                            | Excellent          |

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>65% 50-65% 25-50% <25% Excollent Good Fair Poer

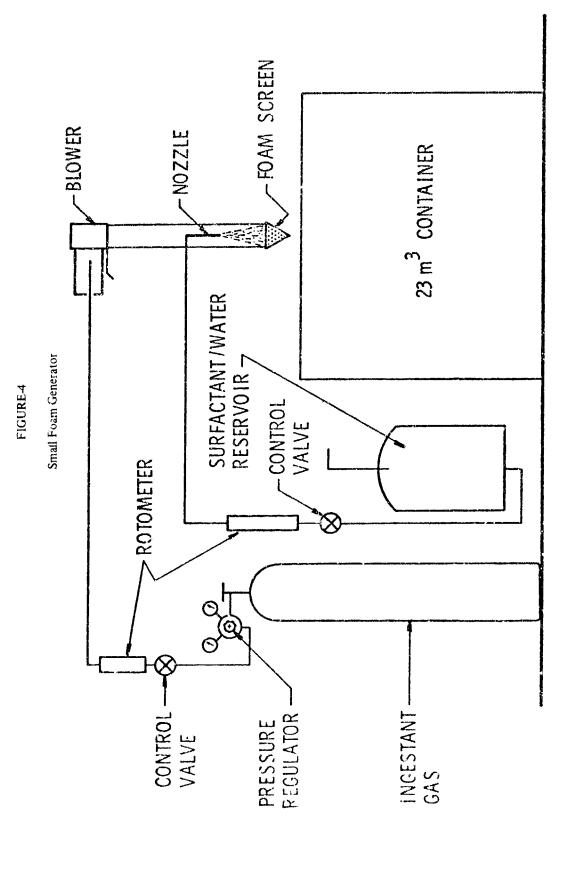
<sup>\*</sup>Foam Stability Rating Based on the Amount of Foam Still Intact 30 Minutes After It Had Been Generated.

millimeters of water in the bottom of a small mixing bowl used with a Hobart high shear mixer. The surfactant manufacturer's recommended percent of surfactants was added to the water and then the unit was turned on and allowed to expand to its maximum ratio. This usually occurred in a matter of seconds. The approximate volume of this expanded foam was measured and a ratio between the original 500 cc and expanded volume was recorded as the expansion ratio. The foam was then allowed to stand for 30 minutes to determine its stability. Foams which decayed to a volume of less than 15% were considered to have poor stability; those that had a volume of between 25% and 50% of the original volume after 30 minutes were considered to be fair; those that measured between 50 and 65% were rated as having good foam stability and those that had a final volume in excess of 65% were considered to be excellent.

Only one surfactant, Hi-Ex, manufactured by Walter Kidde Co., had an excellent foam stability rating in this test series. The final volume of this foam was between 66% and 75% of the original volume after 30 minutes. This surfactant also generated the highest expansion ratio foam.

None of the ingestants were introduced into Hobart generated aqueous foams at this time. It was believed that the higher expansion ratio foams should be considered for further investigation. The only exceptions were the two surfactants supplied by Mearl Chemical, Mearl High Expansion and Mearl Non-Conducting. These surfactants were eliminated because of excessive cost in comparison to surfactants with equal or better form generating capability.

In order to investigate the compatibility of aqueous foams generated with the different surfactants, a small foam generator was constructed for this program. Figure 4 shows a schematic of this foam generator. It consisted of a pressurized bottle from which a mixture of surfactant and water could be introduced, a small squirrel-cage blower and a foam generating screen. This system was set up so that the ingestant gases and powders could be introduced into the intake of the blower and the



ahead of the foam screen. The metering valves were placed in the liquid and gas flow line so that a predetermined rate of flow could be obtained. A rotometer was also placed in the liquid flow line so that an accurate measurement of the quantity of the fluid flow was obtained. This system worked quite effectively and served as a method of screening a large number of samples without expending a great deal of surfactant, ingestant gas and/or man-hours of effort in conducting the tests.

The expansion ratio was determined by capturing a .23 cubic meter volume of foam and accurately measuring the weight of this foam volume. The expansion ratio was then calculated as the weight ratio between an equivalent quantity of liquid being introduced to the weight of the foam. The results of these tests are presented in Table 10. Three of the foams had either good or excellent foam stability and expansion ratio in excess of 250:1.

The Light Water surfactant manufactured by 3M had an expansion ratio of 500:1 in foam stability; however, it required a 6% solution of surfactant which appeared to be excessive when compared to either NCF 865-16J supplied by Mearl or the Hi-Ex supplied by Walter Kidde Co. The other surfactants tested in this system were not considered to be acceptable because they had either poor or fair foam stability.

In both the Hobart and the small foamer surfactant tests, the ratio of surfactant to liquid was varied from that recommended by the manufacturer. However, it was found that the optimum expansion ratio was obtained with the manufacturer's recommended surfactant to water ratio.

As indicated earlier, aqueous foams have been developed primarily for firefighting. The two leading companies who manufacture equipment for dispensing aqueous foams are National Foam Systems, Inc. and the alter Kidde Co. Both of these were contacted to determine if they had equipment which could be adapted for use on this project. It was

TABLE 10 SURFACTANT TEST WITH SMALL FOAMER

|            |              |                  |   | Ratio, %<br>Surfactant | Approximate<br>Expansion | FOOT.        |
|------------|--------------|------------------|---|------------------------|--------------------------|--------------|
|            | Surfactant   | Manufacturer     | Type & Class                                      | Water                  | Ratio                    | Stability*   |
| <u> </u>   | Duponal C    | DuPont           | Anionic - Sodium Lauryl Sulfate                   | 2                      | 100:1                    | Poor         |
| 5.         | Duponal EP   | DuPont           | Anionic - Fatty Alcohol<br>Alhylolamine Sulfonate | 2                      | 100:1                    | Poor         |
| ະກັ        | Triton CF 10 | Rohm & Hass Co.  | Nonionic - Alkylaryl Polyether                    | 83                     | 250:1                    | rair         |
| 4          | Triton X 100 | Rohm & Hass Co.  | Nonionic - Iso-octyl Phenyl<br>Polyethoxyethanol  | ю                      | 250:1                    | Fair         |
| ທ່         | Triton X 151 | Rohm & Hass Co.  | Nonionic - Alkylaryl Polyether                    | м                      | 250:1                    | ក<br>មា<br>ក |
| .9         | NCF 865-16J  | Mearl Chemical   | Nonionic - Unknown                                | 1.5                    | 250:1                    | Good         |
| L.,        | Light Water  | 3M               | Unknown - Fluorocarbon                            | 6.0                    | 500:1                    | Poog         |
| ∞ <b>.</b> | Hi-Ex        | Walter Kidde Co. | Nonionic - Unknown                                | 1.5                    | 1000:1                   | Excellent    |
|            |              |                  |   |                        |                          |              |

\* Foam Stability Rating Based on the Amount of Foam Still Intact 30 Minutes After It Had Been Generated.

| >65%      | 50-65% | 25-50%                   | <25% |
|-----------|--------|--------------------------|------|
| Excellent | Good   | \$=<br>'m'<br>'03<br>LL. | Poor |

determined that the Walter Kidde Co., Model No. P-501A, capable of generating 141.6 cubic meters of foam per minute, met our requirements. This equipment was rented on a lease-purchase agreement and ultimately was purchased as part of this contract and is now the property of the U.S. Army.

The initial effort using this equipment was to evaluate the three candidate surfactants for possible use with this equipment. The results of this study are presented in Table 11. As indicated, the Hi-Ex material supplied by Walter Kidde Co. had the maximum expansion ratio and the best foam stability. Thus, this surfactant was selected for most of the large-scale tests on this program.

## Ingestant Compatibility Test

The initial test to determine the compatibility of aqueous foams to the various ingestant gases was conducted using the small foam generator. The results of these tests are shown in Table 12. As can be seen, the first three tests involved the generation of aqueous foam with air only, and no ingestant gas was supplied to the system. The expansion ratio of this foam was approximately 1,000:1. The test indicated that a concentration of nitrogen gas below 7% had no effect on the expansion ratio of the aqueous foam; however, a concentration of 19% reduced the expansion ratio to approximately 800:1. Concentrations of approximately 1% of Halon 122 allowed a 1,000:1 expansion ratio, but concentrations of 3% and 7% reduced the expansion ratio to 700:1. A 2% concentration of carbon dioxide had no effect on the expansion ratio; however, 13% reduced the ratio to approximately 600:1. This was probably caused by the cooling effect of the expanded carbon dioxide. Concentrations of 2% of argon had no effect on the expansion ratio, and concentrations of 7% of sulphur hexafluoride reduced the expansion ratio to 500:1.

Field tests with various ingested materials were conducted using the large foam generator. The results of these tests are discussed as follows:

TABLE 11 SURFACTANT TEST WITH LARGE FOAMER

|     | Surfactant  | Manufacturer     | Type & Class           | Ratio, %<br>Surfactant<br>Water | Approximate<br>Expansion<br>Ratic | Foam<br>Stability* |
|-----|-------------|------------------|------------------------|---------------------------------|-----------------------------------|--------------------|
| ;   | NCF 863-16J | Mearl Chemical   | Nonionic - Unknown     | 1.5                             | 250:1                             | Cood               |
| 2.  | Light Water | 3M               | Unknown - Fluorocarbon | 0.9                             | 500:1                             | goog               |
| 53. | 3. Hi-Ex    | Waiter Kidde Co. | Nonionic - Unknown     | 1.5                             | 1000:1                            | Excellent          |
|     |             |                  |                        |                                 |                                   |                    |

\*Foam Stability Rating Based on the Amount of Foam Still Intact 30 Minutes After It Had Been Generated.

Excellent >65% Good 50-65% Fair 25-50% Poor <25%

TABLE 12
INGESTANT GAS COMPATABILITY WITH AQUEOUS FOAM\*

|      |                | Ingestant                 |           |           |
|------|----------------|---------------------------|-----------|-----------|
| Test | Ingestant      | Gas Flow Rate,            | Ingestant | Expansion |
| No.  | Gas            | <u>M<sup>3</sup>/Min.</u> | Gas, %    | Ratio     |
| 1    | None           |                           | 0         | 1000:1    |
| 2    | None           |                           | 0         | 1000:1    |
| 3    | None           |                           | 0         | 1000:1    |
| 4    | Nitrogen       | 0.040                     | 3         | 1000:1    |
| 5    | Nitrogen       | 0.040                     | 3         | 1000:1    |
| 6    | Halon 122      | 0.017                     | 1         | 1000:1    |
| 7    | Carbon Dioxide | 0.028                     | 2         | 1000:1    |
| 8    | Carbon Dioxide | 0.028                     | 2         | 1000:1    |
| 9    | Argon          | 0.028                     | 2         | 1000:1    |
| 10   | Argon          | 0.028                     | 2         | 1000:1    |
| 11   | Nitrogen       | 0.096                     | 7         | 1000:1    |
| 12   | Nitrogen       | 0.250                     | 19        | 800:1     |
| 13   | Carbon Dioxide | 0.178                     | 13        | 600:1     |
| 14   | Carbon Dioxide | 0.178                     | 13        | 600:1     |
| 15   | Halon 122      | 0.042                     | 3         | 700:1     |
| 16   | Halon 122      | 0.099                     | 7         | 700:1     |
| 17   | Sulfur Hexa-   | 0.093                     | 7         | 500:1     |
|      | fluoride       |                           |           |           |
| 18   | Sulfur Hexa-   | 0.093                     | 7         | 500:1     |
|      | fluoride       |                           |           |           |
| 19   | Halon 1301     | 0.099                     | 8         | 500:1     |
| 20   | Halon 121      | 0.099                     | 7         | 800:1     |
|      |                |                           |           |           |

<sup>\*</sup>Aqueous foam generated with small foam generator at a rate of approximately 1.42 M<sup>3</sup>/Min. using Hi-Ex surfactant.

## Test No. 1

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - None
Ingestant gas or reagent concentration - ()
Total foam generating time - 90 seconds
Foam generating time with ingestant - not applicable
Approximate foam generated - 210 cubic meters.

REMARKS: This test was conducted to evaluate the foam-generating capability of the Walter Kidde equipment. The test was conducted outdoors. The initial pile of foam generated was approximately 1.2 M high in the center, 18 M in diameter, and took on the shape of a flat-topped dome. There was a 6-knot wind at the time the foam was generated, and it was estimated that less than 5% of the foam was blown away from the site. The foam was very stable and was capable of being generated in an open space without having confining walls. Approximately 30 minutes after the foam was generated, over two-thirds of it was still intact and no evidence of reduction in stability was indicated.

#### Test No. 2

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - None
Ingestant gas or reagent concentration - 0
Total foam generating time - 90 seconds
Foam generating time with ingestant - not applicable
Approximate foam generated - 210 cubic meters.

REMARKS: The test conditions for Test No. 2 were identical to those set up in No. 1; however, at this time, an Army Jeep (M-151) was driven into the foam to determine if the aqueous foam would cause the engine to hesitate, miss, or completely stop. Since the foam is used as a firefighting medium, it was thought that possibly the cooling effect of the foam might quench the engine or that the foam might serve as a

restriction to the flow of air to the engine. Neither of these occurred and the Jeep engine continued to operate within the foam as well as it did outside the foam, probably because the cooling fan of the radiator broke a great deal of the foam before it was able to be ingested into the engine.

#### Test No. 3

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Hydrochloric acid
Ingestant gas or reagent concentration - 9.1%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 45 seconds
Approximate foam generated - 34 cubic meters.

REMARKS: 38 liters of 32% hydrochloric acid were mixed with 95 liters of water. The resulting concentration was 9.1% hydrochloric acid and 90.9% water. Foam was generated with non-contaminated water for 15 seconds to establish a pattern of good foam generation, then a valve connecting the inlet to the pump on the Walter Kidde equipment was turned so that the hydrocloric acid mixture was introduced into the system. Immediately after introducing this mixture to the foamer, the quality of the foam degenerated and the foam generation rate was reduced from approximately 140 cubic meters per minute to 3 or 6 cubic meters per minute. Most of the hydrochloric acid mixture was discharged from the foamer in the form of liquid.

### Test No. 4

Surfactant - 6% Light Water

Ingestant gas or reagent - Hydrochloric acid

Ingestant gas or reagent concentration - 9.1%

Total foam generating time - 30 seconds

Foam generating time with ingestant - 15 seconds

Approximate foam generated - 34 cubic meters

REMARKS: The same test procedure was followed as described in Test No. 3, the only difference being that the fluorocarbon surfactant was used in place of the Hi-Ex. The results were almost identical to those in Test No. 3 in that the hydrochloric acid solution caused the foam generation to cease when the solution was introduced into the system.

### Test No. 5

Surfactant - 1-1/2% NCF 865-16J
Ingestant gas or reagent - Hydrochloric acid
Ingestant gas or reagent concentration - 9.1%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 15 seconds
Approximate foam generated - 34 cubic meters.

<u>REMARKS</u>: Again, as in Tests Nos. 3 and 4, once the hydrochloric acid solution was introduced in the foamer, the foam generation ceased. From this limited set of data, it appears that it would be extremely difficult to generate a stable foam with any of the surfactants which are compatible with the Walter Kidde foam generator. Hence, attempts to introduce hydrochloric acid solutions into the system were abandoned for this test series.

## Test No. 6

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 2%
Total foam generating time - 20 seconds
Foam generating time with ingestant - 20 seconds
Approximate foam generated - 42 cubic meters

REMARKS: A 950 liter propane tank was rented and attached to the Walter Kidde foam generating system. A liquid discharge line which withdrew propane from the bottom of the tank was connected to a manifold that had

4 discharge ports which introduced the propane to the Walter Kidde foam generating equipment, immediately behind the 0.9-meter diameter blade. Care was taken so that a minimum amount of propane was discharged to the atmosphere and virtually all gas was drawn through the foam generating screen system. The vapor pressure of propane at  $21^{\circ}$ C is  $87,184 \text{ kg/M}^2$ . Since this pressure is far in excess of atmospheric pressure, the liquid rapidly volatizes and causes a gas after being discharged from the pressurized tank. Because of this rapid volitization, it was noted that the piping by the manifold on the system became quite cold and frost was formed approximately 10 seconds after the discharge of the propane was initiated. For this reason, a relatively short run time of 20 seconds was conducted. A calculation of the explosive power of the propane gas which ir r fect makes a fuel/air bomb was made. It was determined that if a quantity of this gas were to be detonated it would be in excess or the allowable amount which could be exploded on the grounds of SwRI. Therefore, these tests were conducted at Camp Bullis, a military reservation just north of San Antonio.

The quality of foam generated was very good and the foam generation rate appeared to be the same with the propane gas as it was with only air. After the foam was generated, tests were conducted to determine whether the propane/air-generated foam would actually detonate or even burn. It was found that it would do neither, and we were unable to initiate flame propagation with either a spark or a roadside flare which was drawn through the pile of foam.

The percent of propane that was introduced into the system was determined by monitoring the level of the liquid propane remaining in the 950 liter reservoir after each test. It was determined that the flow rate of the exhaust manifold system was approximately 0.7 liters of liquid propane per second.

Test No. 7

Surfactant - 1-1/2% Hi-Ex Ingestant gas or reagent - Propane Ingestant gas or reagent concentration - 2%

Total foam generating time - 20 seconds

Foam generating time with ingestant - 20 seconds

Approximate foam generated - 42 cubic meters

<u>REMARKS:</u> The test with propane was repeated, and no flame propagation was obtained.

### Test No. 8

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 20 seconds
Foam generating time with ingestant - 20 seconds
Approximate foam generated - 42 cubic meters

REMARKS: In this test, the throttling valve controlling the rate of flow of propane to the system was opened so that an increased amount of propane could be introduced. Again, frost was formed on the exhaust manifold at the end of 10 to 20 seconds. This time, when the flare was thrown into the foam, the foam ignited and the pile was completely consumed within 6 seconds. There was no explosion, but simply a rapid burning.

#### Test No. 9

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 53 seconds
Foam generating time with ingestant - 53 seconds
Approximate foam generated - 113 cubic meters

<u>REMARKS:</u> Again, a flare was thrown into the pile of foam which ignited. The entire volume was consumed within 6 or 7 seconds without detonation.

#### Test No. 10

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 80 seconds
Foam generating time with ingestant - 80 seconds
Approximate foam generated - 170 cubic meters

REMARKS: A great deal of frost was formed on the exhaust manifold by the end of the test. An 8-hp Briggs and Stratton engine mounted on a small cart was towed through the pile of foam. The engine hesitated as though it was going to die, but continued to run, missing badly. The engine was then pulled clear of the foam and it began to run smoother and regained its original speed. A flare was thrown into the pile of foam and approximately 50% of the foam was consumed by burning; the remaining foam did not burn. This indicated to us that a poor mixture of propane and air was present in the foam, probably caused by freezing of the inlet lines because of rapid expansion of the propane.

#### Test No. 11

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 40 seconds
Foam generating time with ingestant - 40 seconds
Approximate foam generated - 85 cubic meters.

REMARKS: The 8-hp spark ignition engine was towed through the foam; this time the engine died 8 seconds after it was introduced into the foam. The engine was towed out of the foam and did not restart. After a period of cranking, the engine started again. A flare was thrown into the pile of foam, and the foam completely burned within 9 seconds. For

the first time, the flame associated with the burning of this foam was visible. This indicated to us that the mixture of propane and air was approximately of the right proportions.

## Test No. 12

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - unknown
Total foam generating time - 40 seconds
Foam generating time with ingestant - 40 seconds
Approximate foam generated - 85 cubic meters

REMARKS: This test was run approximately 15 minutes after Test No. 11; however, when the engine was pulled into the foam, it continued to run haltingly but would not stop even though it was left standing in the foam for approximately 30 seconds. When the engine was pulled clear of the foam, a flare was thrown into the foam, and only 20% to 30% of the foam burned, again indicating a poor mixture of propane and air. After examining the valving and manifold system which introduces the propane to the foam generator, it was concluded that ice was being formed in the throttling valve and/or the exhaust manifold which caused a restriction in the line, thus reducing the quantity of propane that was being introduced into the foam.

### Test No. 13

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 30 seconds
Approximate foam generated - 70 cubic meters

REMARKS: This test was an the day after Test No. 12. When the 8-hp engine was towed through the foam, it died within 7 seconds. After the

engine was towed from the foam, a flare was thrown into the pile and, in 3-1/2 seconds the total volume of foam was burned.

#### Test No. 14

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 30 seconds
Approximate foam generated - 70 cubic meters

REMARKS: The 8-hp engine was towed into the foam and 8 seconds later it died. The total volume of foam burned with 4-1/2 seconds after the flare was introduced into the pile. These tests indicated that it was quite critical that the propane concentration be uniform throughout the foam. In order to minimize the amount of frost that was generated in the propane lines, it was decided to make some modifications, which were accomplished, and tests were conducted during Test No. 15.

#### Test No. 15

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 30 seconds
Approximate foam generated - 70 cubic meters

REMARKS: A 15-meter coil of 1.9-cm diameter copper tube was placed in the propane line between the storage tank and the discharge manifold. This coil of copper tube was placed in a 210-liter drum which was filled with water and the water was heated to 90°C. In this way, the system served as a heat exchanger to reduce the amount of frost which was built up by the rapid expansion of propane. The 8-hp engine was towed into

the foam and died in 8 seconds. The pile of foam was ignited and burned within 6 seconds after the introduction of the flare.

#### Test No. 16

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 30 seconds
Approximate foam generated - 70 cubic meters

REMARKS: This test was conducted approximately 20 minutes after Test No. 15 and the water temperature in the heat exchanger had dropped to 83°C. The quality of the foam appeared to be as good as that generated on Test No. 15, and there was no frost apparent on the exhaust manifold. The 8-hp engine died 10 seconds after it was introduced into the foam, and the foam burned completely in 6 seconds after the flare was put into the pile.

#### Test No. 17

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 30 seconds
Approximate foam generated - 70 cubic meters

REMARKS: This test was conducted 15 minutes after Test No. 16. The water temperature in the heat exchanger had dropped to 79°C. As in Test No. 16, the quality of foam generated was very good. When the engine was drawn through the pile of foam, it died in 8 seconds. The pile of foam burned completely 9 seconds after the flare was introduced into the foam.

#### Test No. 18

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Gasoline
Ingestant gas or reagent concentration - 10%
Total form generating time - 30 seconds
Foam generating time with ingestant - 15 seconds
Approximate foam generated - 30 cubic meters

REMARKS: Since propane is a hydrocarbon and it is effective in stopping the engine, another hydrocarbon was evaluated for its possible use as an ingestant to the foam. The most readily-available hydrocarbon to the field test site was gasoline. Therefore, provisions were made to introduce raw gasoline into the water pump. This was done by modifying the intake line and introducing an aspirator which would draw a 10% solution of gasoline into the water. A valve was put on this line so that the introduction of gasoline into the system could be controlled. Aqueous foam was generated for approximately 15 seconds at the normal rate before gasoline was introduced. The gasoline immediately killed the foam and only a water and gasoline liquid was discharged from the foam generating unit.

#### Test No. 19

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Gasoline
Ingestant gas or reagent concentration - 5%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 30 seconds
Approximate foam generated - 30 cubic meters

REMARKS: Again, the foam generator was operated on 100% water to establish good foam generating characteristics and then the throttling valve was opened so that a quantity of gasoline was introduced into the system which would form a 5% solution of gasoline and water. Again, the foam was killed immediately, and no gasoline and water foam was generated.

#### Test No. 20

Surfactant - 6% Light Water
Ingestant gas or reagent - Gasoline
Ingestant gas or reagent concentration - 5%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 30 seconds
Approximate foam generated - 30 cubic meters

<u>REMARKS:</u> The surfactant was changed on this test; however, the same results occurred, i.e., no satisfactory foam could be generated with the gasoline being introduced.

### Test No. 21

Surfactant ~ 1-1/2% Hi-Ex
Ingestant gas or reagent ~ Gasoline
Ingestant gas or reagent concentration ~ 5%
Total foam generating time ~ 15 seconds
Foam generating time with ingestant ~ 15 seconds
Approximate foam generated ~ 0

REMARKS: 5.7 liters of gasoline were mixed with 108 liters of water and 1 liter of tall oil acid. This solution was thoroughly stirred and mixed so that an emulsified blend of gasoline and water was generated. This mixture was introduced to the foam generator and no foam was generated.

## Test No. 22

Surfactant ~ 1-1/2% Hi-Ex
Ingestant gas or reagent - Gasoline
Ingestant gas or reagent concentration - 5%
Total foam generating time - 15 seconds
Foam generating time with ingestant - 15 seconds
Approximate foam generated - 0

REMARKS: The surfactant, 1.9 liters of Hi-Ex was added to the blend of water and gasoline and tall oil acid to form an emulsion and surfactant solution. This was then pumped to the foam generator. No foam was generated with this system. At this point, it was decided to abandon the gasoline ingestant system.

#### Test No. 23

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Iodine
Ingestant gas or reagent concentration - 2%
Total foam generating time - 40 seconds
Foam generating time with ingestant - 40 seconds
Approximate foam generated - 10 cubic meters

REMARKS: 0.7 kilograms of iodine crystals were dissolved in 3.8 liters of isopropylalcohol. This solution of iodine and alcohol was thoroughly mixed with 190 liters of water. This mixture was pumped through the foam generator and virtually no foam was generated. The small quantity that was generated had very coarse bubbles and was not stable.

#### Test No. 24

Surfactant - 1-1/2% Hi-Ex
Ingestant gas or reagent - Propane
Ingestant gas or reagent concentration - 5%
Total foam generating time - 30 seconds
Foam generating time with ingestant - 30 seconds
Approximate foam generated - 70 cubic meters

REMARKS: a 6-hp, self-propelled, riding lawnmower was driven through the foam, and the engine died in approximately 7 seconds. This identical test series was repeated 10 additional times and, in each case, the engine died within an average of 8 seconds.

#### Summary - Foam Investigations

As a result of this test series conducted with the large foam generator, it was determined that an aqueous foam containing approximately 5% propane is capable of consistently killing a spark ignition engine contained in a small, self-propelled, riding lawnmower. Also, as illustrated by the feasibility demonstration, this system was effective in stopping a one-half ton pickup truck powered by an SI engine. Successful tests were run with the vehicle hood open and also with the hood closed; however, with the hood closed it took a slightly longer time for engine interference to occur.

#### CONCLUSIONS

The following conclusions were reached as a result of this program:

## A. Engine Combustion Interference

- Several gaseous and liquid agents which caused engine interference were identified.
- Several mechanisms of CI engine interference were proposed.
- Halon materials were demonstrated to function as "heat sink" agents in causing CI engine interference.

### B. Lubricant Interference

- No short-term catastrophic lubricant interference was observed.
- Several interferants showed potential for long-term lubricant interference.

# C. Ingestant Dispensing System

- High expansion ratio water-based foam containing propane as the interferant was a very effective system for stopping both small and larger scale spark ignition engines.
- The feasibility of a foam + interferant system was proven.
- Optimization of this system and application to larger scale SI and CI engines should be considered for the next phase of this project.

#### RECOMMENDATIONS

It is felt that the results of this investigation could be expanded to a large scale to include vehicles the size of a mility tank. It is recommended that additional tests be conducted with a Walter Kidde foam generator to make certain that this conclusion is valid. The possibility of obtaining an even larger foam generator should be considered for the next phase of this project. It is also recommended that additional effort be considered for identifying and demonstrating the use of field available interferant agents such as engine exhaust gases in combination with foam.